THERMAL DECOMPOSITION OF EXPLOSIVES BELOW THE MELTING POINT

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Upon investigation of the thermal decomposition of tetryl below
the melting point Farmer[1] showed that the condensed products of the
decomposition reaction of tetryl dissolve it. Then Hinshelwood[2] dev-
eloped a mathematical analysis for a decomposition reaction taking
into account the appearance of a liquid phase in the process of de-
composition. However, in deriving the equation, Hinshelwood made
assumptions which mutually excluded one another. Thus, calculating
the ratio of the solid and the liquid phases in the decomposition pro-
cess, he assumed (according to Raoult's law) that at constant tempera-
ture the concentrations of material in the liquid phase, being in
equilibrium with the solid phase, are constant. Also, calculating the
concentration of catalyst in the liquid phase, Hinshelwood assumed it
to be proportional to the degree of transformation. .

Considerably later Bawn[3] examined decompositions of organic ex-
plosives with "melting under the melting point in the process of the
reaction" in the simplest case of two monomolecular reactions.

In the present work various cases of decomposition of solid ex-
plosives taking into account the appearance of a liquid phase are con-
sidered. In the following it has been assumed in every instance that
the original explosive dissolves in the reaction products and that the
thermodynamic equilibrium between the solid and the liquid phases is
successfully established. Consequently, the ratio of concentration of
the original substance C_{B_L} to the products of the reaction C_{A_L} in the

liquid phase $a = C_{B_L} / C_{A_L} = B_L / A_L$ is a constant value at a constant

temperature and is not dependent on the degree of transformation up to
the moment of disappearance of the solid phase.

The degree of transformation η_i is equal to

Under the condition that the density of the reaction products
is little different from the density of the original substance one can
write $A_0 = B_0 (1 - \mu)$, where $\mu = \dfrac{v_{initial} - v_{final}}{v_{initial}}$

(the degree of change in volume at complete decomposition); B_0 - init-
ial quantity of explosive; A_0 - the total quantity of condensed react-
ion products. The quantity B in the solid phase is $B_s = B - B_L$.

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Up to the moment of complete solution $A = B_o (1 - \mu) \eta$;

$$B_L = B_o a(1 - \mu) \eta \, ; \quad B_s = B_o (1 - \eta_i) - B_o a(1 - \mu) \eta$$

If in the solid and the liquid phases the decomposition reaction proceeds according to a first order equation then the overall rate is defined by the following expression

$$-\frac{dB}{dt} = \frac{1}{1 - \mu} \frac{dA}{dt} = k_1 C_{B_{TB}} v_{TB} + k_2 C_{B_{\varkappa}} v_{\varkappa} = k_1 B_{TB} + k_2 B_{\varkappa}.$$

where v_s and v_1 are the volumes of the solid $\underline{/TB/}$ and the liquid phases $\underline{/\varkappa/}$, respectively.

The dependence of the rate on the degree of transformation is given by the expression

$$\frac{d\eta_i}{dt} = k_1 (1 - \eta_i) - k_1 a (1 - \mu) \eta_i + k_2 a (1 - \mu) \eta_i =$$

$$= k_1 + [a (1 - \mu)(k_2 - k_1) - k_1] \eta_i.$$

Defining $a(1 - \mu) (k_2 - k_1) - k_1 = k_m$, we obtain $\frac{d\eta_i}{dt} = k_1 + k_m \eta_i.$

At $a(1 - \mu) (k_2 - k_1) > k_1$ and $k_2 > k_1$ the overall reaction rate will increase proportionally to the degree of transformation up to the moment of complete solution of the original substance in the reaction products. After the moment of complete solution the reaction will proceed according to the ordinary first order equation

$$\frac{d\eta_i}{dt} = k_2 (1 - \eta_i).$$

The solid phase disappears when the degree of transformation is η_i'

$$B_{TB} = 0 = B_0 (1 - \eta_i') - B_0 a (1 - \mu) \eta_i', \quad \eta_i' = \frac{1}{a(1 - \mu) + 1}.$$

At this moment $k_1 + k_m \eta_i^1 = k_2 (1 - \eta^1)$.

Equation (1a) upon integration gives $k_m t = \ln \frac{k_1 + k_m \eta}{k_1}$.

Kinetic curves calculated according to equation (3) have a clearly expressed S - shaped form (at the value $a(1 - \mu) (k_2 - k_1) > k_1$).

The curve for the dependence of the rate on the degree of transformation possesses a characteristic appearance when calculated according to equation (1) and to the classical equation of a first order reaction (Fig. 1.)
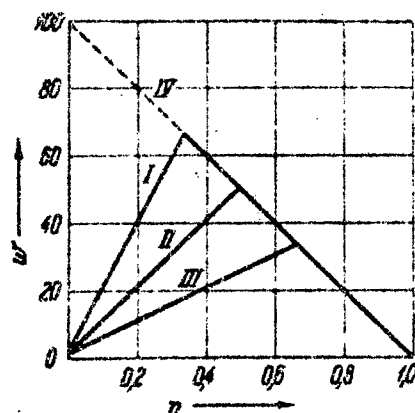
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Fig. 1. Dependence of reaction rate on the degree of transformation calculated according to equation (1), when $k_1 = 1$, $k_2 = 100$, $\mu = 0.9$. Parameter a equals 20 for I, 10 for II, and 5 for III. The straight line IV is drawn according to the equation of a first-order reaction.

Maximum rate is attained in this case at the point of complete solution, when $\tau_i = \tau_i^{\ 1}$.

In a case in which the condensed decomposition products can act as catalysts, the expression for the overall rate of reaction must be written as follows:

$$-\frac{dB}{dt} = \frac{1}{1-\mu} \frac{dA}{dt} =$$

$$= k_1 C_{B_{тв}} v_{тв} + k_2 C_{B_ж} v_ж + k_3 C_{B_ж} C_{A_ж} v_ж =$$

$$= k_1 B_{тв} + k_2 B_ж + k_3 B_ж C_{A_ж};$$

C_{A_L} — the concentration of catalyst in the liquid phase; $C_{A_L} = \alpha A / v_L$;

α — fraction of catalyst in the condensed reaction products;

$$v_ж = B_ж = A = A(1-a), \quad C_{A_ж} = \frac{\alpha}{1+a}.$$

Thus, the rate of reaction up to the moment of complete solution in the case of catalysis by the condensed end products is defined by the expression.

$$\frac{d\tau_i}{dt} = k_1 + \left[k_2 a(1-\mu) + \frac{k_3 \alpha (1-\mu) a}{1+a} - k_1 a(1-\mu) - k_1 \right] \tau_i.$$

$$k_2 a(1-\mu) + \frac{k_3 \alpha (1-\mu) a}{1+a} - k_1 a(1-\mu) - k_1 = k'_m;$$

$k_m^{\ 1}$ — quantity, dependent only on the temperature and constant in the decomposition process when $t = $ const. Consequently, even in the case of catalysis by the condensed end products one obtains an expression analogous to equation (1) for a reaction proceeding according to the

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first order law:

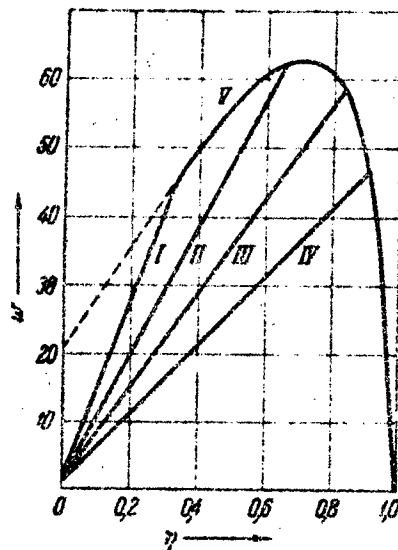$$\frac{d\eta_i}{dt} = k_1 + k'_m \eta.$$

Fig. 2. Dependence of reaction rate on the degree
of transformation calculated according to equation
(4), when $k_1 = 1$; $k_2 = 20$, $k_3 a = 100$, $\mu = 0.9$. Parameter a is equal to 20 for I, 5 for II, 2 for III,
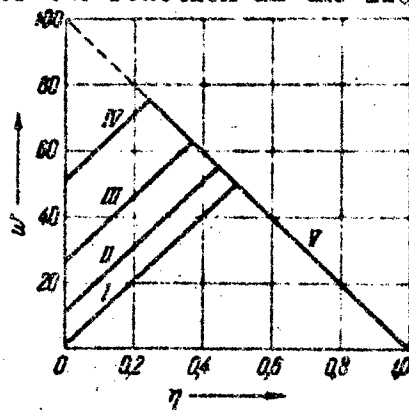and 1 for IV. Curve V is drawn according to equation (5) for the reaction in the liquid phase.

Fig. 3. Dependence of reaction rate on the degree
of transformation calculated according to equation
(6), when $k_1 = 1$, $k_2 = 100$, $\mu = 0.9$, a = 10. Ratio
T/B_0 for the straight lines I, II, III, and IV is
equal to 0, 0.01, 0.025, and 0.050, respectively.
The straight line V is drawn according to the equation for a first order reaction.

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Equation (4a) differs from (1a) only in the value of k_m.

After the moment of complete solution, which occurs when $\eta_1 = \dfrac{1}{a(1-\mu)+1}$, the process of decomposition obeys the equation obtained earlier[4] for the case of autocatalyzed decomposition of liquid explosives under conditions in which the volume of the condensed phase is variable:

$$\frac{d\eta}{dt} = k_2(1-\eta_i) + k_3 a(1-\mu)\frac{\eta(1-\eta)}{1-\mu\eta} .$$

The dependence of reaction rate on the degree of transformation calculated according to equations (4) and (5) is represented in Fig. 2. It is evident from the diagram that the maximum reaction rate can lie at the point of complete solution of the original substance or later as the reaction proceeds even in absence of the solid phase.

It is very interesting to note the influence of impurities, even chemically inert, which can increase the rate of decomposition of the explosive by transforming part of it into the liquid phase (in a case, in which the eutectic temperature of the system original explosive – inert impurity lies below the experimental temperature). The rate of decomposition even in this case will be equal to the sum of the rates in the solid and in the liquid phases (in the solid and in the liquid phase monomolecular reactions take place)

$$W = k_1 C_{B_{TB}} v_{TB} + k_2 C_{B_{\varkappa}} v_{\varkappa} = k_1 B_{TB} + k_2 B_{\varkappa},$$

T – inert impurity;

$$v_{\varkappa} = A + B_{\varkappa} + T, \quad A = B_0(1-\mu)\eta_i,$$

$$B_{\varkappa} = B_0(1-\mu)a\eta_i + Ta, \quad B_{TB} = B_0 - B_0\eta_i - B_0(1-\mu)a\eta_i - Ta,$$

where $a = \dfrac{B_L}{A+T}$ (solubility of substance B in T and in mixtures A + T is constant).

The reaction rate as a function of the degree of transformation can be written in the following manner:

$$\frac{d\eta}{dt} = k_1 + (k_2 - k_1)\frac{T}{B_0}a + \underbrace{[(1-\mu)a(k_2 - k_1) - k_1]}_{k_m}\eta_i .$$

Thus, even in this case the decomposition rate is directly proportional to the degree of transformation up to the moment of complete solution, after which it falls according to the first order law, but the initial rate is directly proportional to the quantity of impurities or admixtures and the solubility of the original explosive in it (Fig. 3.).

In a case in which the solubilities of the explosive in the inert impurity and in the reaction products are different one can easily obtain a suitable relationship for the solubility from the composition of the system and use it when deriving equation (6).

At the point of complete solution of the original substance in the reaction products the solid phase disappears and the law for the re-

action process changes. It is known that for an ideal system

$$\ln N = -\frac{\lambda(T_{пл} - T)}{RT_{пл}T},$$

where N — mole fraction of the dissolved substance; λ — heat of fusion; T_F — melting point $\boxed{\text{пл}}$ temperature; T — experimental temperature. Consequently, on basis of equation (2) the degree of transformation, at which the complete solution takes place, is decreased by increasing the temperature according to the following law

$$\eta' = \frac{1-N}{1-\mu N} = \frac{1 - \exp\left(-\dfrac{\lambda(T_{пл}-T)}{RT_{пл}T}\right)}{1 - \mu \exp\left(-\dfrac{\lambda(T_{пл}-T)}{RT_{пл}T}\right)}.$$

Thus, assuming the establishment of thermodynamic equilibrium between the solid and the liquid phases in the decomposing explosive - reaction products system, we were successful in obtaining equations fundamentally describing the phenomena observed in the thermal decomposition of explosives at a temperature below the melting point.

It is necessary to bear in mind that in real systems one can observe more complex cases linked with the complex mechanism of the chemical reaction of decomposition. However, it is always necessary to examine possibilities of progressive solution of the original explosive in the reaction products with a corresponding change in laws of kinetics for the reaction process.

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